

Synthesis and Properties of Periodic Copolymers: Alternating Copolymerization of Propylene with Methyl α -Chloroacrylate

Tadamichi HIRABAYASHI and Kenji YOKOTA

*Department of Materials Science and Engineering, Faculty of Engineering,
Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466, Japan*

(Received April 4, 1988)

ABSTRACT: To synthesize a series of periodic copolymers containing simple α -olefins, the alternating copolymerization of propylene (P) with methyl α -chloroacrylate (MCA) was examined. An alternating P-MCA copolymer could hardly be obtained by conventional procedures where organoaluminium chlorides alone were used as complexing reagents. The addition of vanadium oxytrichloride or acetylacetonate as the second catalyst provided the well-defined alternating P-MCA copolymer. The P(P-*alt*-MCA) was found to have coisotacticity (σ) of 0.67 by NMR analysis and glass transition temperature (T_g) of 56°C by DSC.

KEY WORDS Propylene / Methyl α -Chloroacrylate / Alternating Copolymerization / Poly(propylene-*alt*-methyl α -Chloroacrylate) / Vanadium Oxytrichloride / Vanadium Acetylacetonate / Glass Transition Temperature /

In order to study structure-property relationships, the authors synthesized copolymers well-designed with respect to sequence order, namely periodic copolymers.¹⁻⁵ It is possible to polymerize some olefinic hydrocarbons with acrylic esters or nitriles in an alternating manner in the presence of Lewis acids such as ethylaluminium sesquichloride, which is now generally called "Lewis-acid complexed alternating copolymerization method." Hirooka *et al.*⁶ listed up several α -olefin monomers, including propylene and ethylene, which are available for the above method.

However, almost all investigators thereafter have been concerned with hydrocarbon monomers having a large Q -value such as 1,3-dienes and styrene derivatives. As for the alternating copolymers prepared from unconjugated α -olefin with polar vinyl monomers, however, little has been noted.⁷ Hence, their alternating structures have been poorly characterized, and their physical properties

little studied.

In this paper, we describe how to synthesize a new alternating copolymer of propylene and methyl α -chloroacrylate, as well as its configurational microstructure and a few thermal properties.

EXPERIMENTAL

Materials

Monomers. Methyl α -chloroacrylate (MCA) was synthesized according to the literature,⁸ washed with aqueous sodium hydrogen sulfite, water, aqueous sodium hydroxide and water, dried over calcium hydride, and distilled after prepolymerization, bp 49–50°C/38 mmHg. Methyl acrylate (MA) was purified in the same manner as MCA. Propylene (P) was commercially available as the purest grade and used without further purification.

Catalyst. Commercial ethylaluminium sesquichloride (EASC) and diethylaluminium

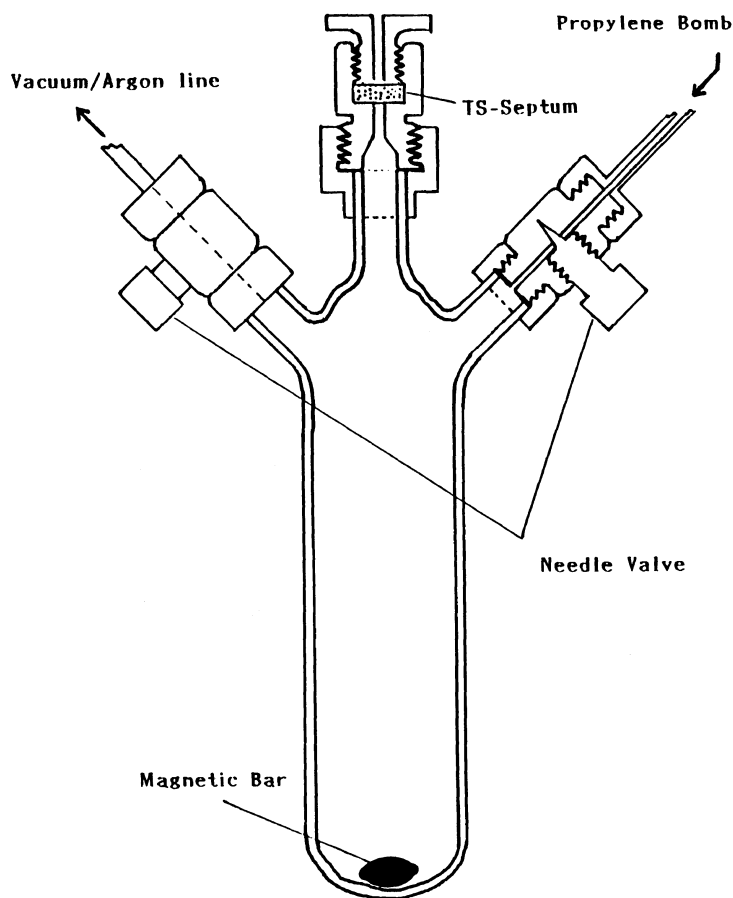


Figure 1. Glass pressure vessel for polymerization.

chloride (DEAC) were distilled under reduced pressure of nitrogen atmosphere, and used as ca. 4 mol dm^{-3} solution in toluene or *n*-hexane. Vanadium oxytrichloride $[\text{VOCl}_3]$ was the commercially purest grade and used as solution in hydrocarbon. Commercial vanadium acetylacetonate $[\text{V}(\text{acac})_3]$ was recrystallized from acetylacetone under a nitrogen atmosphere.

Solvent. Toluene and *n*-hexane were conventionally purified, dried over sodium and distilled just prior to polymerization.

Polymerization

A typical procedure is described as follows. After displacement by dry argon, in a 100 ml

glass pressure vessel illustrated in Figure 1, definite amounts of MCA and toluene were added through a septum and, by opening a needle valve, P (gas) were allowed to liquefy at -78°C . After closing the valve, the calculated amount of EASC, and then VOCl_3 were added at once through the septum. After polymerization for an adequate period at -78°C , propylene was released by vaporization at -20°C . The reaction vessel was reset in dry box, the septum was removed and 15 ml of methanol was carefully poured into the vessel at -78°C . To this mixture was further added a large excess of methanol containing hydroquinone. Resulting crude copolymer was collected by centrifugation, reprecipitated from

Alternating Copolymer of Propylene with MCA

Table I. Copolymerization of propylene (P) and methyl α -chloroacrylate (MCA) or methyl acrylate (MA) with organoaluminium chloride alone at -78°C

No.	Monomer (mmol)		Al ^a -Solvent	Al/MCA	Feeding mode ^b	Time h	Polymer				
	P	MCA or MA					Yield/g	<i>s</i> -THF/g ^c	P/%	$[\eta]$ /dl g ⁻¹ ^e	
1	969	MCA	51.3	EASC-Heptane	0.49	A	1	0.23	None	0	
2	622		51.3	EASC-Heptane	1.02	A	5	4.61	None	0	
3	942		51.3	DEAC-Toluene	1.00	A	3	0.04			
4	868		51.3	DEAC-Toluene	0.31	A	20	0.30	None	0	
5	897		47.4	EASC-Heptane	1.00	B	6	0.79	0.21	43.2 ^d	
6	724		40.5	EASC-Heptane	1.01	B	6	0.66	0.09	18.0 ^d	
7	1200	MA	53.4	EASC-Heptane	1.00	A	1	2.41	—	48.7	2.96
8	868		53.4	EASC-Heptane	1.00	A	0.5	0.64	—	46.0	2.80

^a EASC, $(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3$; DEAC, $(\text{C}_2\text{H}_5)_2\text{AlCl}$.

^b Detailed explanation was given in text. Mode A, $(\text{MCA or MA} + \text{Al}) \rightarrow \text{P}$; B, $(\text{P} + \text{Al}) \rightarrow \text{MCA}$.

^c Soluble fraction in THF.

^d Determined by ^1H NMR for THF soluble fraction.

^e Determined in CHCl_3 at 25°C .

chloroform (CHCl_3) solution in methanol. The fraction insoluble in tetrahydrofuran (THF) was separated off, while the soluble copolymer was reprecipitated in methanol twice, and dried *in vacuo*.

Analyses

NMR spectrum was measured on Hitachi R-24A (60 MHz) or Varian XL-200 instrument (200 MHz for ^1H and 50 MHz for ^{13}C). The IR spectrum was recorded on a JASCO IR-E. Intrinsic viscosity of copolymer was determined in CHCl_3 at 25°C with an Ubbelohde viscometer. Gel permeation chromatography (GPC) in THF was recorded on a Toso HLC-803D equipped with TSK GMX-, G1000-, G2000-, and G4000-HXL columns at 37°C . The column system was calibrated with standard polystyrene samples. Elemental analysis was carried out on a Yanagimoto CHN-MT-1S. Differential scanning calorimetry (DSC) was measured in the range of -150 to 50°C on a Rigaku-Denki Thermoflex with a low temperature unit. Thermogravimetry (TG)

was also measured on the same instrument in air.

RESULTS AND DISCUSSION

Copolymerization of P and MCA Catalyzed by Organoaluminum Chlorides Alone

Results of copolymerization of P and MCA in the presence of EASC or DEAC are summarized in Table I, which clearly demonstrate that organoaluminum chlorides alone could not give a well-defined alternating copolymer of P and MCA. Polymers obtained in this system were mostly MCA homopolymer. This was different from the case of P and MA described in the previous work,⁶ and also in the present study (last two lines in Table I). MCA homopolymer was almost insoluble in THF, and often showed a shoulder peak at 1765 cm^{-1} in IR spectrum, suggesting that 5-membered lactone was partially formed during polymerization or work-up procedures, as is shown by eq 1.⁹

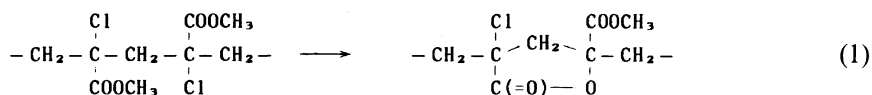


Table II. Copolymerization of propylene (P) and methyl α -chloroacrylate (MCA) with $(C_2H_5)_3Al_2Cl_3$ (EASC)–transition metal compounds (M)^a

No.	Monomer (mmol)		Catalyst (mmol)			Feeding mode ^e	Polymer				
	P	MCA	EASC	M	M/EASC		Yield/g	MCA/%	<i>s</i> -THF/g ^c	MCA/%	$M_n \times 10^4$ ^f
9	651	23.7	24.0	V(acac) ₃	0.12	C ₁	2.18	64.1	1.89	59.2	
10	738	25.7	26.0	VOCl ₃	0.11	C ₁	1.85	61.5	1.37	53.0	
11	738	25.7	26.0	V(acac) ₃	0.10	C ₂	0.38	8.0	0.31	7.4	35.0
12	738	25.7	26.0	V(acac) ₃	0.10	D	1.95	59.1	1.72	55.6	6.2
13	738	25.7	26.0	VOCl ₃	0.11	D	2.67	54.6	2.50	51.9	5.9
14	738	25.7	26.1 ^b	VOCl ₃	0.11	D	2.33	81.9	0.86	58.5	2.5
15	738	25.7	30.8	VOCl ₃	0.09	D	1.10	46.9 ^d	—	—	
16	738	25.7	26.0	Cr(acac) ₃	0.10	D	0.07	75.4	—	—	
17	664	23.7	23.6	TiCl ₄	0.10	D	0.06	90.5	—	—	

^a Polymerization conditions: temp, -78°C ; time, 24 h.^b As Al compound, $(C_2H_5)_2AlCl$ was used.^c See text. Mode C₁, (Al+P)→MCA→V; C₂, (Al+P)→V→MCA; D, (MCA+P)→Al→M.^d According to ¹H NMR spectrum, approximately equimolar mixture of PMCA and PP.^e Soluble fraction in THF. Composition was estimated by ¹H NMR and partly elemental analysis.^f Determined by GPC.

Judging from the poor solubility, intermolecular esterification also must occur though there was not clear evidence for that in its IR spectrum because of overlapping with absorption due to a pendant ester group.

When the mixing order was changed from (MCA+Al)→P mode, which means MCA and an organoaluminum compound were mixed in advance and then P was added, to the (P+Al)→MCA mode where MCA was finally fed, a small amount of fraction soluble in THF was found to contain P-units, however, far apart from 1:1 composition. It does not seem that the given conditions can regulate the sequence order of the copolymer alternating.

Copolymerization of P and MCA Catalyzed by EACS–Vanadium Compounds

Results of copolymerization of P and MCA in the presence of organoaluminum chlorides with some transition metal compounds are summarized in Table II. EASC–VOCl₃ and –V(acac)₃ were effective to produce copolymers, while Cr(acac)₃ and TiCl₄ could hardly induce polymerization. The crude copolymers soluble in CHCl₃ had been still contaminated

with some MCA homopolymer. However, most of the copolymers were soluble in THF, too, in contrast to the solubility of PMCA mentioned above. This desirable behaviour in the solubility suggests that an alternating structure of P and MCA units might be predominant and lead to avoidance of lactonization (or intermolecular esterification) between adjacent substituents on homosequence of MCA.

Actually, reprecipitation from THF solution in methanol under ice-cooling brought about copolymers of approximately 1:1 composition of P and MCA units. Pouring of butyl acetate/butyl benzoate (85/15) solution into carbon tetrachloride was also effective to remove PMCA. The soluble part was allowed to reprecipitate in methanol, resulting in a more closely 1:1 composition of copolymer. Figures 2(a), 3, and 4 show ¹H, ¹³C NMR, and IR spectra of a sample (No. 13), respectively. The ¹H NMR spectrum entirely differed from that of the equimolar mixture of two homopolymers PMCA and PP (atactic), as shown in Figure 2(b). A resonance of methylene protons in the alternating samples centered at 2.0 ppm.

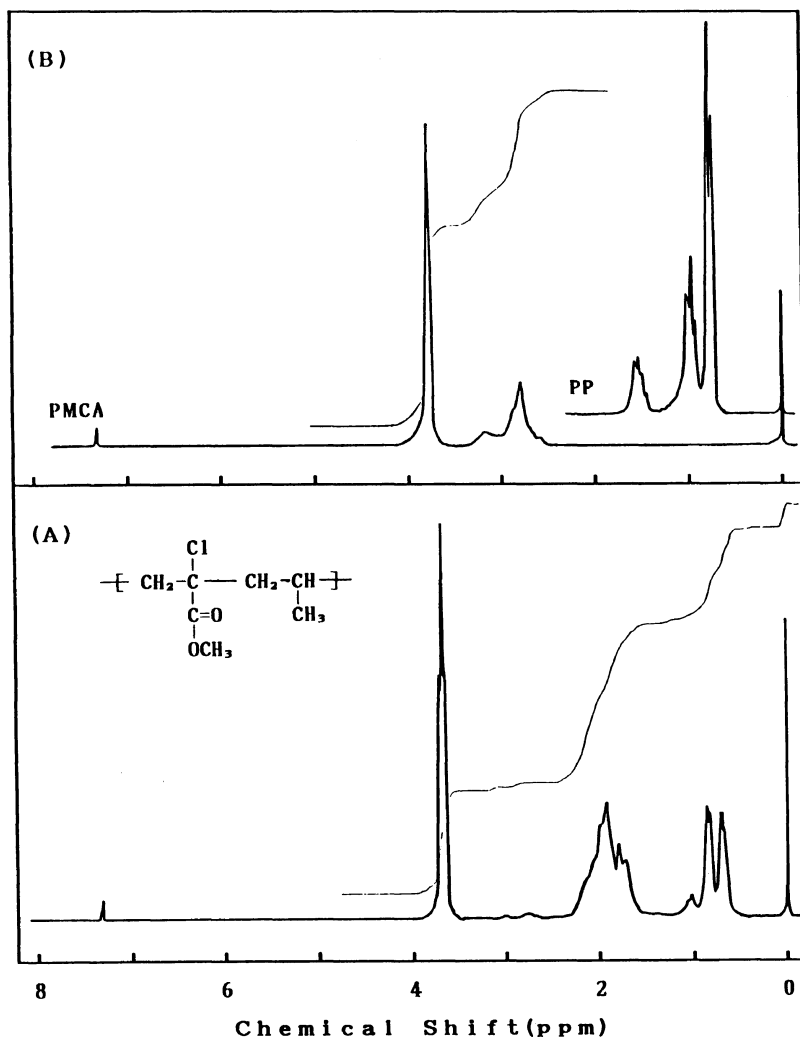


Figure 2. ^1H NMR (200 MHz) spectra of (A) P(P-*alt*-MCA) prepared from Exp. 13, and (B) PP and PMCA in CDCl_3 . Hexamethyldisiloxane was used as the internal standard.

Methyl protons in the P unit split into three peaks due to different magnetic anisotropy with larger difference (~ 28 Hz) in chemical shift. These resonances should be assigned as the structure of P(P-*alt*-MCA). Also the ^{13}C NMR spectrum was reasonably assignable to P(P-*alt*-MCA).

In addition to using EASC/ VOCl_3 or $\text{V}(\text{acac})_3$ as catalysts, their order of mixing was important to obtain the most reliable alternating copolymer of P and MCA. The mixing

order of the (MCA + P) \rightarrow Al \rightarrow V mode was preferred to that of (P + Al) \rightarrow V \rightarrow MCA and (P + Al) \rightarrow MCA \rightarrow V modes. Preliminary mixing of MCA with EASC tended to cause homopolymerization of MCA even if any co-catalyst was added to the mixture later. On the other hand, preliminary mixing of EASC and vanadium compounds followed by introduction of P led to rapid homopolymerization of P, where a Ziegler-Natta type of species active to propylene must be formed. The addition of

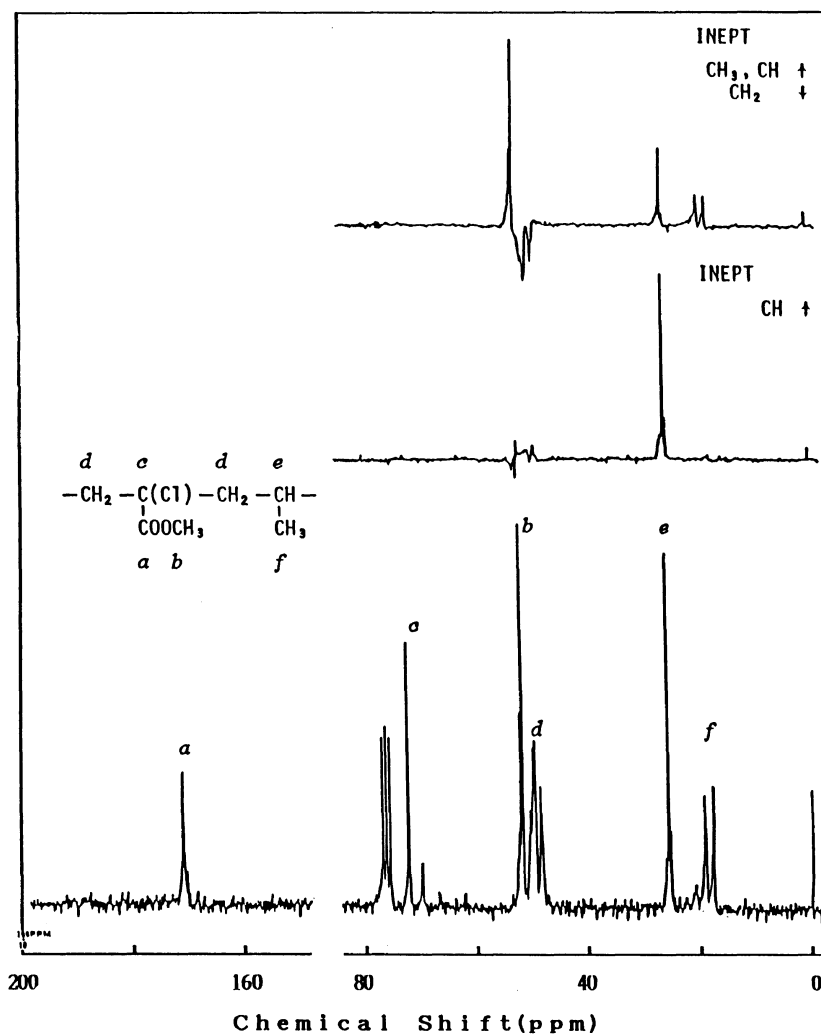


Figure 3. ^{13}C NMR (50 MHz) spectrum of P(P-*alt*-MCA) prepared from Exp. 13 in CDCl_3 , and assignments.

a fairly excess of EASC to MCA in exp. 15 was also accompanied by homopolymerization of P. This could be explained by the same reason. A similar phenomena with respect to the mixing order has been already found^{10,11} in alternating copolymerization of P-butadiene, P-isoprene and acrylonitrile(AN)-butadiene catalyzed by organoaluminium halides- VOCl_3 , and monodentate (P, AN) and bidentate (1,3-dienes) ligands must certainly be coordinated alternately onto active vanadium

species.

Anyhow, EASC-vanadium compounds system was ascertained to be not merely effective to polymerize AN-butadiene alternately but also MCA-P. Both situations were very similar. However, MCA was generally classified as a monodentate ligand. The alternating copolymer in this work involving one of acrylic esters might be caused by MCA behaving as a bidentate ligand. A speculative mechanism containing a chelated ester group is proposed

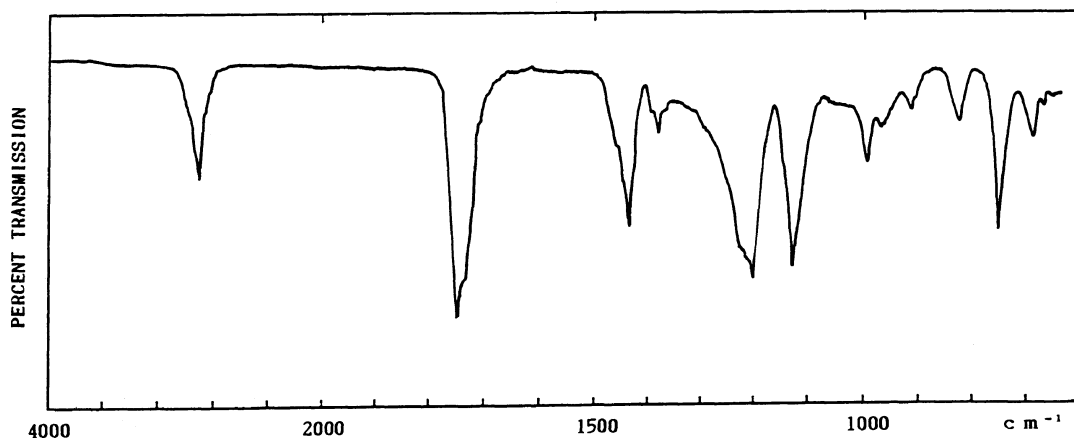
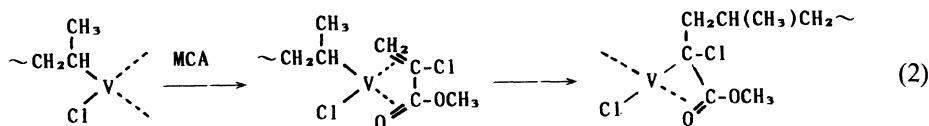


Figure 4. IR spectrum of the most reliable sample of P(P-alt-MCA).

in eq 2.



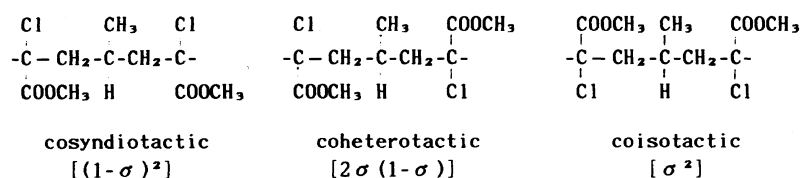
Since P and methyl methacrylate (MMA) could never give any alternating copolymer under the same conditions, the chlorine atom in MCA may play an important role in controlling the coordination number of the catalyst ion instead of the oxygen atom. In this connection, it should be noted that using DEAC instead of EASC in exp. 14 resulted in poor yield of the alternating copolymer. It reminded us of the fact that, in living polymerization of P catalyzed by $\text{V}(\text{acac})_3 - (\text{C}_2\text{H}_5)_n\text{AlCl}_{3-n}$,¹² the content of chlorine atoms in the catalyst system is important to polymerize P successfully. However, it is difficult to discuss further the mechanism of the alternating regulation at this stage.

The molecular weight (M_n) of P(P-alt-MCA) was estimated by GPC as 6.2×10^4 and 5.9×10^4 for samples No. 12 and 13, respectively. Molecular weight distribution for both

samples was considerably narrow, the M_w/M_n ratio being about 1.3 according to GPC. However, P(P-alt-MA) solution in CHCl_3 was found extremely viscous, suggesting that its M_n must be larger than that of P(P-alt-MCA).

Microstructure of the Alternating Copolymer of P and MCA

From ^1H and ^{13}C NMR spectra of the most reliable sample of P(P-alt-MCA), coisotacticity (σ) could be estimated in the same manner as described previously.¹³ Methyl protons on P unit were split into three peaks in ^1H NMR spectrum (Figure 2) and should be assigned to cosyndio-, cohetero-, and coisotactic P-centered triads illustrated below in the increasing order of magnetic field. On the basis of the intensity ratio (9:47:44) of those signals, σ was determined as 0.66 as an average.



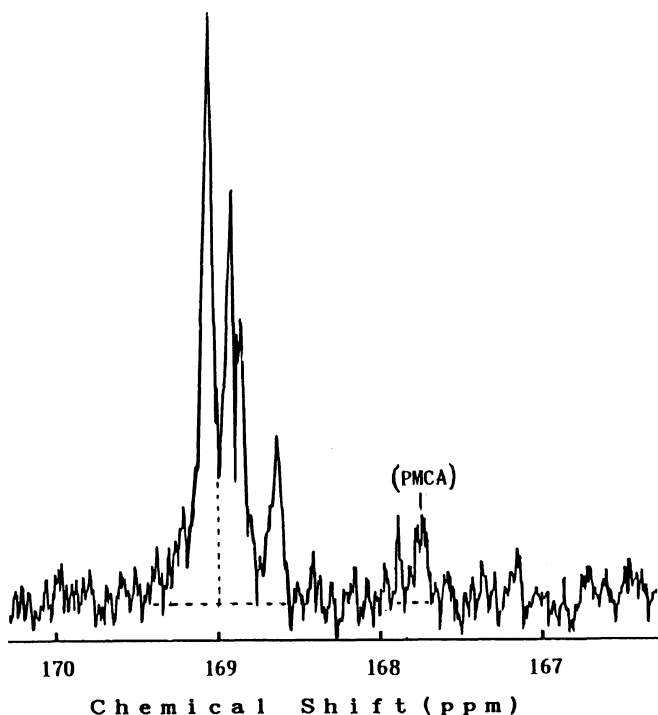


Figure 5. ^{13}C NMR spectrum expanded the range of 166–170 ppm in Figure 3. See text for assignment of each peak-group.

Methyl carbons were split into three peaks in ^{13}C NMR spectrum, too. The intensity ratio (9:46:45) in the increasing order of magnetic field was very close to that of ^1H NMR spectrum. Figure 5 shows the expanded spectrum of carbonyl carbon region in ^{13}C NMR. Three peak-groups among 168.5–169.5 ppm appeared in the intensity ratio of 45.5:43.6:10.9, and were assignable to coiso-, cohetero-, and cosyndiotactic MCA-centered triads in the increasing order of magnetic field. Again, σ was determined as 0.67_4 as an average in agreement with the result from ^1H NMR.

Thermal Properties of the Alternating Copolymer of P and MCA

DSC curves of the most reliable P(P-*alt*-MCA) samples were measured and the glass transition temperature (T_g) was determined as the midpoint of curve-inflection, 56°C , during cooling. According to Fox's equation,¹⁴ apply-

ing 87°C for T_g of PMCA and -1°C for PP, the predicted T_g for the equimolar copolymers or mixture composed of P and MCA units was found as 60°C . Both T_g found and calculated are very close to each other. The T_g values of the homopolymers in this case were measured under the same DSC conditions as P(P-*alt*-MCA). Such homopolymers could be often obtained in the course of the present work. Although alternative T_g values of the homopolymers were found in the literature as 105°C ¹⁵ for PMCA and -20°C ¹⁶ for PP, these were not used to predict the T_g of the alternating copolymer.

Figure 6 shows the TG curves of (a) P(P-*alt*-MCA) [No. 13], (b) PP, and (c) PMCA. The thermal stability of P(P-*alt*-MCA) resembled rather PP than PMCA except for the temperature of the onset of depolymerization.

Acknowledgement. The authors wish to

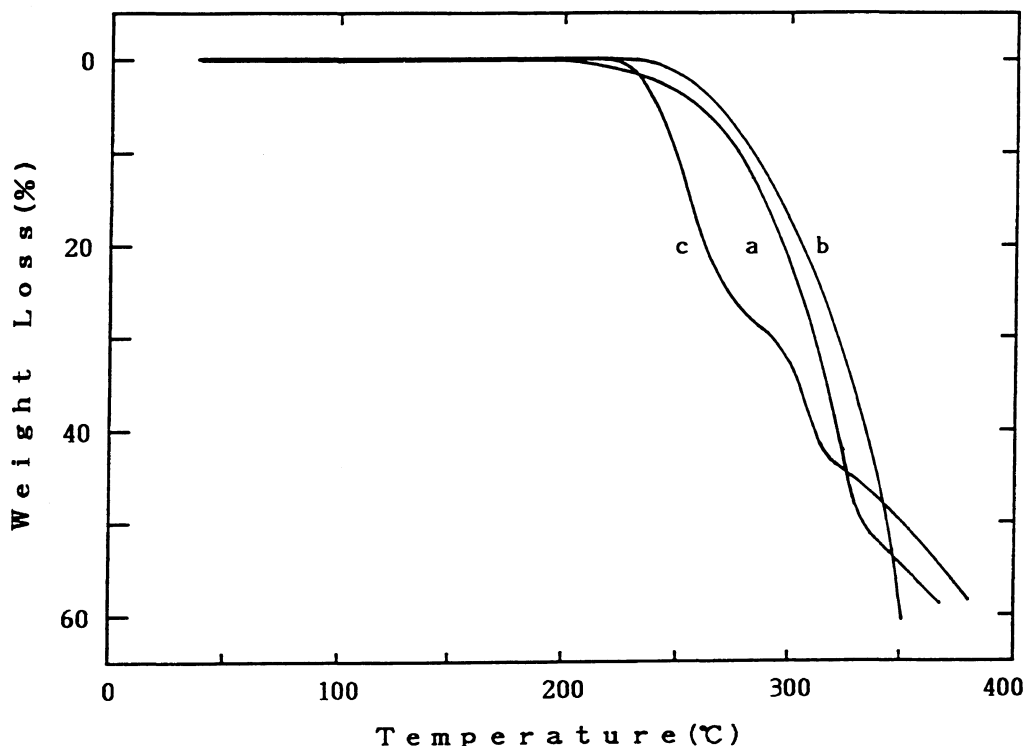


Figure 6. Thermogravimetric curves of a, P(P-alt-MCA); b, PP (atactic); and c, PMCA prepared from Exp. 13, -11, and -2, respectively.

thank Iwata Chemical Industry Co., Ltd. for the research grant.

REFERENCES

1. K. Yokota and T. Hirabayashi, *Macromolecules*, **14**, 1613 (1981).
2. K. Yokota, T. Kougo, and T. Hirabayashi, *Polym. J.*, **15**, 349 (1983).
3. K. Yokota, T. Kougo, and T. Hirabayashi, *Polym. J.*, **15**, 891 (1983).
4. K. Yokota and T. Hirabayashi, *Polym. J.*, **17**, 991 (1985).
5. T. Hirabayashi, T. Itoh, and K. Yokota, *Polym. J.*, **20**, 1041 (1988).
6. M. Hirooka, H. Yabuuchi, S. Kawasumi, and K. Nakaguchi, *J. Polym. Sci.*, **11**, 1281 (1973).
7. A. L. Logothetis and J. M. McKenna, *J. Polym. Sci., Chem. Ed.*, **15**, 1431, 1441 (1977).
8. C. S. Marvel, J. Dec, H. G. Cook, and J. C. Cowen, *J. Am. Chem. Soc.*, **62**, 3495 (1940).
9. B. K. Patnaik and N. G. Gaylord, *J. Polym. Sci. B*, **9**, 347 (1971).
10. J. Furukawa, *Polymer*, **15**, 162 (1974), and many related papers.
11. J. Furukawa, Y. Iseda, K. Haga, and N. Kataoka, *J. Polym. Sci. A-1*, **8**, 1147 (1970).
12. Y. Doi, S. Ueki, and Y. Keii, *Macromolecules*, **12**, 814 (1979).
13. T. Hirabayashi and K. Yokota, *J. Polym. Sci., Chem. Ed.*, **14**, 45 (1976).
14. T. G. Fox, *Bull. Am. Phys. Sci.*, **1**, 123 (1956).
15. E. A. W. Hoff, D. W. Robinson, and A. H. Willbourn, *J. Polym. Sci.*, **18**, 161 (1955).
16. R. F. Boyer, *Rubber Chem. Technol.*, **36**, 1303 (1963).